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<p>(21) International Application Number: PCT/US82/00363 (22) International Filing Date: 25 March 1982 (25.03.82) (31) Priority Application Numbers: 249,043 360,516 (32) Priority Dates: 30 March 1981 (30.03.81) 22 March 1982 (22.03.82) (33) Priority Country: US (71) Applicant: ATLANTIC RICHFIELD COMPANY [US/US]; 515 S. Flower Street, Los Angeles, CA 90071 (US). (72) Inventors: CLOUGH, Thomas, J. ; 22515 Peale Drive, Woodland Hills, CA 91364 (US). MACKENZIE, John, D. ; 2456 Arbutus Drive, Los Angeles, CA 90049 (US).</p>	<p>(74) Agents: BECKER, Stanley, A. et al.; Legal Department, Atlantic Richfield Company, 555 17th Street, Denver, CO 80202 (US). (81) Designated States: DE, FI, FR (European patent), GB, JP. Published With international search report.</p>	
<p>(54) Title: GLASS COMPOSITIONS, PRODUCTS AND METHOD OF FORMATION FROM NATURAL ZEOLITES</p> <p>(57) Abstract</p> <p>A glass composition is formed from a mixture comprising one or a plurality of natural mineral zeolites and has a melting point in the range of from about 1000° to about 1500°C. The glass compositions of this invention can be formed into various glass articles, including flat glass, glass containers, glass fiber and glass foam.</p>		

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TITLE: GLASS COMPOSITIONS, PRODUCTS AND METHOD OF FORMATION
FROM NATURAL ZEOLITES

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FIELD OF THE INVENTION

10 The invention herein relates to glasses. While it pertains to glasses generally, it has particular pertinence to glasses which are fiberizable.

BACKGROUND OF THE INVENTION

15 The natural mineral zeolites are a group of hydrous alkali and/or alkaline earth aluminosilicates which have an open three-dimensional crystalline framework. While a large number of individual mineral zeolites are known and have been described in the literature, eleven minerals make up the major group of mineral zeolites: analcime, chabazite, clinoptilolite, 20 erionite, ferrierite, heulandite, laumontite, mordenite, natrolite, phillipsite and wairakite. The chemical and physical properties of these major mineral zeolites, as well as the properties of many of the minor mineral zeolites, are described extensively in Lefond (ed.), 25 Industrial Minerals and Rocks (4th edn., 1975), pp. 1235-1274; Breck, Zeolite Molecular Sieves (1974), especially Chapter 3; and, Mumpton (ed.), Mineralogy and Geology of Natural Zeolites, Vol. 4 (Mineralogical Society of America: November 1977). These publications 30 also describe the geologic occurrence of the natural mineral zeolites and some industrial and agricultural uses which have been proposed or in which the natural mineral zeolites are now being used commercially.

35 It is important to note that the natural mineral zeolites are an entirely different class of materials from the "synthetic zeolites" which have been widely described in many recent articles and patents. Because there is no universally recognized system for



5 naming the synthetic zeolites, and because some of the synthetic materials exhibit x-ray diffraction patterns which suggest possible similarities in structure with the natural mineral zeolites, some reports in the literature and patents have described certain synthetic zeolites as "synthetic" versions of the natural mineral zeolites. Thus, for instance, certain synthetic zeolites have been described as "synthetic analcime" or "synthetic mordenite" and so forth. As noted in the
10 aforementioned Breck reference, however, this approach is technically unsound and has merely led to confusion between the two otherwise distinct classes of materials: the natural mineral zeolites and synthetic zeolites. While it has been recognized that there are structural
15 similarities between the two groups, it is clear that the natural mineral zeolites constitute a class of materials significantly separate and distinct in structure and properties from the synthetic zeolites.

Glasses are vitreous materials composed largely
20 of silica. Because silica is a highly refractory material, however, substantial quantities of soda ash, lime or other fluxing materials are added to the silica to permit the glass forming composition to be melted at reasonable temperatures. Small quantities of other
25 materials, usually elemental materials or oxides, are commonly added to glass melts to provide particular properties such as color or chemical resistance to the finished glass. Heretofore, however, there has not been any report of significant usage of zeolites in glass
30 matrices and particularly as the principal component of a glass matrix. One experiment has been reported in which a clinoptilolite and glass mixture was fired at 800°C (well below the melting point of either) to produce what was described as a porous low density glass
35 composition; see Mumpton, supra, p. 197, referring to Tamura Japanese published application 74/098,817 (1974).

BRIEF SUMMARY OF THE INVENTION

The invention herein is a glass composition



formed from a molten mixture which mixture prior to melting comprises a natural mineral zeolite and which has a melting temperature in the range of from about 1000° to about 1500°C. In a preferred embodiment the natural mineral zeolite comprises mordenite and has a melting point in the range of from about 1250° to about 1400°C. Also included within the scope of the present invention is a glass body formed from the aforesaid glass composition, as well as glass fiber formed from the aforesaid composition.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

In the present invention a mineral zeolite is a principal (preferably major) component of the mixture of raw materials which is melted to form the subject glass composition. As noted above, the various individual mineral zeolites are well described in the published literature. It will be understood that these materials, all being natural, will vary in composition over recognized ranges from batch to batch depending on the particular ore body (or portion of the ore body) from which the zeolites have come. It will also be understood that frequently two or more zeolitic minerals will be mixed in a particular ore body. These normally need not be separated for use in the invention, since this invention contemplates the use not only of individual mineral zeolites but also mixtures of two or more mineral zeolites. In fact in many cases it will be preferred to have a mixture of zeolites since changes in desirable properties, such as melting temperature, can often be obtained by use of such a mixture. Also present will usually be various other minerals, including amorphous materials. The presence of the other minerals does not prevent the mixture from reflecting the properties of the zeolite component.

In the present invention the mineral zeolite or mixture of mineral zeolites to be used will be chosen so as to provide a melting temperature in the range of from about 1000° to about 1500°C, preferably from about 1250°



to about 1400°C. These mineral zeolites thus provide a glassy matrix at a melting temperature generally below that commonly associated with most glasses, particularly the fiberizable glasses.

- 5 Particularly preferred among the mineral zeolites as the raw materials for the glass forming mixtures are mordenite and clinoptilolite. A mixture of these two zeolites, in generally similar proportions (mixed with a lesser amount of amorphous materials and
10 other minerals) has been found to melt in the range of about from about 1250° to about 1400°C. Thus, by itself, it provides an appropriate melting temperature without the need to add any other zeolitic minerals or any chemical fluxes. Suitable mineral zeolites are
15 available commercially from The Anaconda Company.

- The mineral zeolites used to form the glasses of the present invention may be incorporated into the glass forming mixture in amounts which are generally similar to the combined quantities of silica and alumina
20 in convention glass compositions. The common inorganic oxides used in glass compositions to provide such properties as color, resistance to devitrification, thermal stability, resistance to chemical attack and the like may be incorporated along with the mineral zeolites
25 in essentially the same proportions as are used in conventional glass compositions. The proportion of mineral zeolite in the glass forming mixture will be at least 40% by weight and preferably at least about 50% by weight of the composition. It may be desirable in some
30 instances to add small quantities (usually not more than about 30% by weight) of scrap glass ("cullet") to the composition. It will, of course, in this case be necessary to use a cullet which does not have a significant detrimental affect on the finished
35 properties of the zeolite based glass.

Where melting temperature reductions are desired beyond those obtainable by mixture of two or more mineral zeolites, conventional chemical fluxes such



as soda ash may be added.

The glass compositions of this invention may be used to form any of a variety of types of glass bodies and articles. The glass herein is suitable for use as flat glass, container glass (including bottle glass) and so forth. It is common for glasses of this invention to show some color, particularly a light brown. It is believed that this is due to the ferric oxide present in the zeolite composition. If desired, the intensity of a light brown color so present can be diminished or eliminated by extraction of the iron from the zeolite. Alternatively the ferric iron can be reduced to ferrous iron, which will change the color from brown to blue or green. The end use of the glass made from the present glass compositions will determine whether or not color in the glass can be tolerated. The degree of coloration in a particular composition of the present invention will determine, for instance, whether bottles made of the glass will be the clear bottles used for such products as milk or the colored bottles used for products such as beer or toiletries.

The glasses of this invention are particularly useful for the formation of glass fibers. They may be fiberized in any conventional fiberization manner, including melt spinning, extrusion, extrusion followed by gas or steam jet attenuation or centrifugal extrusion followed by gas or steam jet attenuation. As with conventional glass fibers the methods of formation and collection will determine whether the glass fibers are to be used for textiles, as staple fibers or as glass wool, or insulation glass. Materials conventionally used with glass fibers such as coupling agents and polymeric binders may be equally well used with the present glass fibers.

Two properties of the zeolite glasses are especially noteworthy with respect to the glass fiber products. First, as noted above, the zeolites melt at temperatures which are generally some 50° to 150°C lower



than known glass fiber formers such as alkali resistant (zirconia-containing) glass batches and "E-glass" batches. The lower melting temperatures provide significant savings in energy usage, as well as permitting extension of service life of melting equipment such as bushings, since these can be operated at less severe conditions. Second, tests have indicated that the zeolite based glass fibers exhibit a degree of alkali resistance comparable to the zirconia-containing glass fibers. Since the zeolite based glass fibers are significantly less expensive, however, they could be used for a wide variety of reinforcement applications on alkaline environments where the high cost of the zirconia glass fibers now precludes the use of glass reinforcement.

The zeolite glasses of this invention may be formed by melting in conventional glass making furnaces, with the advantageous lower temperature processing discussed above. In addition, the zeolite glass melt does not significantly react with refractory materials of the type commonly used to line such furnaces, thus contributing to extended lining life. The lower melting temperatures of the zeolite glasses also has the advantage of reducing any sulfur emissions from glass melting operations, because sulfur compounds which may be present (as in the refractory furnace lining) have less tendency to break down into gaseous sulfur compounds at the reduced melting temperatures.

The zeolite based glasses of this invention may also be in the form of glass foams.

Also included in the scope of this invention is the formation of glass ceramics from the zeolites. This is accomplished by first forming the vitreous glass from the zeolite melt and then devitrifying the glass with controlled cooling to form ceramics of the desired crystallinity. This aspect of the invention is especially applicable to the fibrous materials, and can be used to convert "500°C service temperature" glass



fibers to "1100°C service temperature" ceramic fibers. Crystalline phases which have been identified in ceramic fibers thus formed from a mordenite raw material are anorthite and diopside. Of particular interest is the ability of these zeolites to form such ceramics without the use of nucleating agents; i.e., the zeolites can be considered "self-nucleating". Nucleating agents can, however, be used if desired to initiate ceramic formation.

The glasses of this invention have coefficients of expansion on the same order as many metals. Therefore, they can be used to line metal shells without incurring inordinate problems of differential expansion.

As an example of the present invention, a glass composition was formed from a mineral zeolite designated "2020A" and commercially available from The Anaconda Company. In this experiment the glass composition was formed entirely from the commercial mordenite mineral, which melted at approximately 1350°C to produce a brown colored glass comprising the following composition, stated in percent by weight on a dry weight basis:

TABLE I

	SiO ₂	61.5%
	Al ₂ O ₃	10.2%
25	MgO	3.8%
	CaO	16.7%
	Na ₂ O	2.1%
	K ₂ O	2.7%
	Fe as Fe ₂ O ₃	3.0%

30

(Note that conventional aluminosilicate glass melting temperatures are on the order of 1600°C.)

Glass of this composition was remelted to form glass fibers and was found to fiberize readily and produce a good quality glass fiber.

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The glass of this example was found to have a bulk density comparable to that of soda-lime (window) glass and E-glass, and a coefficient of thermal



expansion approximately half way between the coefficients of those two glasses. The glass transition temperature was found to be over 10% higher than that of soda-lime glass, indicating a greater degree of stability and resistance to devitrification. An important result determined was that the glass fibers formed had alkali resistance (in 5% NaOH at 90°C) comparable to that of samples of commercial zirconia containing "alkali resistant" glass fibers, as indicated in Table II below:

TABLE II

<u>Weight Loss, %.</u>			
	<u>Zeolite</u>		<u>Commercial</u>
	<u>Glass</u>	<u>"E-Glass"</u>	<u>"Alkali</u>
	<u>Fibers</u>	<u>Fibers</u>	<u>Resistant"</u>
<u>Time, Hrs.</u>			<u>Glass Fibers</u>
24	3.53	28.17	2.10
48	3.97	35.78	4.34
72	5.08	41.94	5.90

It is thus evident that the mineral zeolite glasses of the present invention have properties at least equal to the common glasses and glass fibers of the prior art, can be formed at temperatures substantially below the temperatures used to form prior art aluminosilicate glasses, and show alkali resistant properties comparable to the much more expensive zirconia-containing glasses.

STATEMENT OF INDUSTRIAL APPLICATION

The invention herein is applicable to the formation of glass and glass fibers in common industrial glass and glass fiber making operations. The glasses and glass fibers so formed are themselves used in a wide variety of industrial applications including containers, thermal insulation, fibrous reinforcement and flat glass.

The above discussion is intended to be



generally descriptive of the invention and exemplary of certain embodiments including those preferred. It will be evident to those skilled in the art, however, that there may be numerous other embodiments which are not
5 described above but which are clearly within the scope and spirit of the present invention. It is intended, therefore, that the scope of this invention is to be limited solely by the appended claims.



WHAT IS CLAIMED IS:

1. A glass composition having siliceous and aluminous oxide portions and formed from a molten mixture which mixture prior to melting comprises a natural mineral zeolite component and which has a melting temperature in the range of from about 1000° to about 1500°C.

2. A glass composition as in Claim 1 wherein the source of the siliceous and aluminous oxide portions of said composition comprises said natural mineral zeolite component.

3. A glass composition in Claim 2 wherein said source of the siliceous and aluminous oxide portions of said composition consists essentially of said natural mineral zeolite component.

4. A glass composition as in Claims 1, 2 or 3 wherein said natural mineral zeolite component comprises at least one natural zeolite mineral selected from the group consisting of analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, natrolite, phillipsite, wairakite or mixtures thereof.

5. A glass composition as in Claim 4 wherein said natural mineral zeolite component comprises mordenite, clinoptilolite or mixtures thereof.

6. A glass composition as in Claim 5 wherein said natural zeolite component comprises said mixture of mordenite and clinoptilolite.

7. A glass composition as in Claims 1, 2 or 3 wherein said mixture has a melting temperature in the range of from about 1250° to about 1400°C.

8. An article formed from a glass composition



as in Claims 1, 2 or 3.

9. An article as in Claim 8 comprising flat glass, a container, glass fiber or glass foam.

10. An article as in Claim 9 comprising glass fiber.

11. An alkaline body reinforced with the glass fiber of Claim 10.

12. An article formed from a glass composition as in Claim 5.

13. An article as in Claim 10 comprising flat glass, a glass container, glass fiber or glass foam.

14. A method of forming a glass composition which comprises melting a mixture comprising a natural mineral zeolite component at a temperature in the range of from about 1000° to about 1400°C.

15. A method as in Claim 14 wherein said natural mineral zeolite component comprises at least one natural zeolite mineral selected from the group consisting of analcime, chabizite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, natrolite, phillipsite, wairakite and mixtures thereof.

16. A method as in Claim 15 wherein said natural mineral zeolite component comprises mordenite, clinoptilolite or mixtures thereof.

17. A method as in Claims 14, 15 or 16 further comprising fiberizing said glass composition.

18. A method as in Claims 14, 15 or 16 further comprising foaming said glass composition.



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 82/00363

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL.3 C03B 19/08, 37/01; C03C 3/00, 11/00, 13/00; C04B 7/02		
US. CL. 65/2, 22; 106/99; 501/27, 36, 39, 68		
II. FIELDS SEARCHED		
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Classification System	Classification Symbols	
US	65/2, 22; 106/99; 501/27, 36, 39, 68	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US, A, 3,101,251, Published, 20 August 1963, Howell, See Example V	1-18
A	US, A, 3,666,506, Published, 30 May 1972, Cowan, Jr.	1-18
A	US, A, 3,846,143, Published, 05 November 1974, Mod	1-18
A	US, A, 4,153,439, Published, 08 May 1979, Tomic	1-18
<p>* Special categories of cited documents: ¹⁹</p> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>		
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